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I. OBJECT:

This study is directed at determining factors that play a role in sewage chlorination. This preliminary report outlines some observations and discusses the developing problem.

II. SUMMARY:

1. Control of oxidation appears as a vital factor in conditioning sewage for chlorination.

   a. Initial aeration is very beneficial.
   b. Intermediate aeration is of doubtful benefit.
   *c. Extended aeration brings a large increase in chlorine demand and a corresponding reduction of susceptibility to chlorination.

2. Amino acids increase chlorine demand drastically and interfere seriously with chlorine disinfection. The protein components of sewage are, accordingly, important factors in chlorination.

3. Moderate aeration with sewage bacteria sharply reduces the interference of amino acids with chlorination.

4. Septic sewage is characterized by a very high chlorine demand. Chlorine disinfection is normal after this demand is satisfied.

5. The orthotolidine test for residual chlorine appeared as a satisfactory test for estimating the chlorine requirement for acceptable disinfection of Hyde Park sewage. A high temperature and/or a long period of exposure to chlorine before determining the residual chlorine favored reliability.

III. GENERAL PROCEDURES

The studies have been made with Hyde Park sewage, clarified by treatment with 100 ppm of aluminum sulfate and filtering through coarse filter paper. The normal bacterial population

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*See footnote, page 8

was reduced by pasteurizing, heating to 70°C and holding 10 minutes before cooling in a water bath. Pasteurizing was carried out before filtering to aid clarification. This treatment reduced the normal population to a point where there was no interference. Control counts were made on every sewage sample to make certain that there would be no interference error. A washed suspension of E. coli was added to each sample immediately before test chlorination and the death rate studied by plate counting on nutrient agar. The temperature of testing was 28°C, the room value during this summer period.

Test samples were run at one to several chlorine levels and the data plotted on 5-cycle, semi-log graph paper. The family of curves obtained clearly revealed killing rates over the experimented range.

OT residual chlorine values were used to pick the chlorination range with marked success. A few instances of unusually high killing rates, apparently from sewage bactericidal to E. coli, led to loss of data from some experiments. It is more difficult to pick a good experimental Cl_2 range than to pick a reliable killing range.

All Cl_2 death rate tests were terminated by a sodium thiosulfate quench. This quench was demonstrated to halt the killing reaction, whereas, dilution of the test sample in a water blank permitted considerably more killing after sampling.

IV AERATION STUDIES (Fig. 1, 2, 3, 4,)

Some general trends were soon noted after conducting a series of aeration studies. Slow aeration with sewage bacteria was generally beneficial to the subsequent chlorination process. There is considerable variation between samples, with benefits varying from neglegible to large. Aeration extended beyond 4 to 6 hours lost much of its beneficial effect and, prolonged, began to exert a detrimental influence.

Outstanding benefits from a slow aeration were noted in sewage supplemented with amino acids. This supports the theory that deamination is very beneficial when carried out prior to chlorination. Time has not yet permitted studies of the actual changes occuring in the nitrogenous system. A marked rise in residual chlorine values accompanies the disinfection benefit associated with slow aeration.

The situation has been very different in rapid oxidation by the activated sludge procedure. Nitrites (and probably other intermediate products) appear in the sewage. The OT test now gives a positive reaction without addition of chlorine. The chlorine demand increases to about 5 times the control value and susceptibility to chlorination drops by a corresponding factor. Sludge in a different state of activity may give less nitrite accumulation and less chlorine demand; however, nitrite accumulation is common because of detergents and other sewage components that retard normal nitration. Nitrite destroys Cl_2; nitrate does not destroy Cl_2. Nitrate production is highly variable and not considered important [1].

Some concern has been felt because of the air supply available for these studies. The compressed air has a petroleum-like odor. Comparison with a known pure supply is among projected experiments.

The high demand developed in activated sludge sewage suggested that chlorination should be conducted ahead of the aeration stage when chlorination and sludge treatment must be combined. Chlorination before biological treatment is avoided because of the strong preservative action of chlorine. The prechlorination procedure has been carried out over two weeks, with one part of freshly chlorinated sewage mixed with two parts of activated sludge treated sewage at blending time. It appears that the process can be carried on indefinitely through quenching the chlorinated sewage with strongly oxidized product. This blending order eliminates danger of chlorine toxicity in the effluent. A secondary advantage appears to be exceedingly rapid and complete sludge separation. BOD reduction by the procedure has not been evaluated.

It is anticipated that sewage lagoons will present a difficult problem. Algae in the lagoons will produce amino compounds from the inorganic nitrogen. This will interfere seriously with chlorination. Nitrites that are normally formed during natural oxidation will likewise interfere. It may be essential to chlorinate before lagooning to achieve a practical operation. No trouble is expected from chlorine preservation in the lagoon because the incoming sewage will be quenched by the reservoir of high chlorine demand product in the lagoon.

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[1] Committee Report. Operation and Control of Activated Sludge Sewage Treatment Works. Sewage Works Jour., 14, 3 (1942).

Aeration studies in the laboratory, without special equipment to control rates, have obvious limitations. These studies require extension with pilot plant equipment that can more accurately define test conditions.

V. SEPTIC SEWAGE (Fig. 5)

Sewage held in deep containers varied greatly in the development of the septic condition. The septic condition was generally characterized by a very high chlorine demand, about 4 times that of the control. It is essential to add enough chlorine to saturate the demand before chlorine disinfection takes place. It was clearly demonstrated in one experiment that 32 times as much chlorine was demanded by a septic sample as by the normal control. It is, therefore, extremely important to avoid the development of septic sewage. The product is both a nuisance and not susceptible to chlorination. Moderate aeration appears to be effective for avoiding the septic condition with its nuisance and high chlorine demand factors.

Septic sewage presents some peculiar management problems in the laboratory. Both exposure to air or agitation that permits loss of volatile constituents cause a drastic drop in chlorine demand. One experiment had to be abandoned when it was noted that a septic sample had lost its high demand value during filtration. As nitrogen was not available for displacing oxygen during filtration, subsequent samples were clarified by careful decantation, with minimum agitation. A definite drop in demand value occurs on pasteurization, probably from loss of volatile constituents. Large tanks of septic sewage are much less susceptible to oxidation or loss of volatile constituents.

VI. EFFECT OF AMMONIA SUPPLEMENTS (Fig. 6)

Ammonia is a normal sewage constituent, arising from urea, which hydrolyzes rapidly on exposure to sewage bacteria. Some ammonia additions of 20 to 100 ppm of nitrogen were made to sewage just prior to chlorination studies. The ammonia had from little or no effect to a moderate enhancing effect on chlorination. Ammonia added to a water system, markedly slows chlorination. An observation in the literature [1] reveals that ammonia enhances chlorination in the presence of proteinaceous substances. Simultaneously, our studies were revealing the marked blocking of chlorination by amino acids.

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[1] Geiger, K. H. and Moloney, P. J. Enhanced Effectiveness of Chlorination. Canadian Jour. Pub. Health, 43, 359 (1952).

These observations suggested that sewage treatments that favored deamination would be beneficial. This led to aeration studies on sewage in the presence of sewage bacteria and bacteria settled from the aeration processes. The activated sludge process was utilized (very rapid aeration); slow aeration studies were also carried out. Slow aeration is economical, avoids sepsis and favors facultative bacteria. Slow aeration permits bacterial oxidation of strong reducing compounds that interfere in chlorination. E. coli is known to carry out deamination [1]; this suggests that deamination should be achieved readily in sewage.

VII. EFFECT OF AMINO ACIDS (Fig. 7, 8, 9)

Rudolfs and Gehm [2] studied the effect of amino acids in sewage, but did not report any interference with chlorination.

A zero chlorine demand was noted for glutamic acid. Our observations reveal a marked interference. Glutamic acid sharply increases chlorine demand, particularly after a short period of contact. Marked interference with chlorination has been found with dl-alanine, l-glutamic acid, peptone, l-serine, l-threonine, l-leucine, and l-aspartic acid. L-cystine, a reducing agent as well as amino acid, had about 10 times the chlorine demand of most amino acids. Its effect on chlorine disinfection has not yet been evaluated by us.

It should be noted that slow aeration in the presence of sewage bacteria markedly reduces the chlorine demand of sewage supplemented with amino acids. Proteinaceous substances are important components of sewage.

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[1] Delwiche, C. C. Biological Transformation of Nitrogen Compounds. Ind. and Eng. Chem., 48, 1421 (1956).

[2] Rudolf, W. and Gehm, H. W. Sewage Chlorination Studies. N. J. Agr. Expt. Sta. Bul. 601, N. J. Agr. Expt. Sta., March 1936.

VIII. ANALYTICAL PROCEDURES FOR ESTABLISHING CHLORINE DOSAGE

A difficulty in sewage chlorination has been the determination of chlorine requirement. The orthotolidine method has been the principal test used but many failures have been reported in its application. The iodometric and amperometric procedures have been reported to give results closely paralleling the orthotolidine(OT) method [1]. Oxidation potential procedures have been used with doubtful reliability. A few iodometric determinations were made in these studies along with the OT values, but the procedure required much more time and displayed no advantage.

The OT procedure has been used as a guide to chlorination ranges in these studies. The residual chlorine value has been used exclusively. A review of the runs reveals that the test indicates the chlorine level for acceptable kill quite satisfactorily on Hyde Park sewage. Most estimates of chlorine requirement have been made after 5 minutes of chlorine treatment at 28°C. It was noted that the OT value after 20 minutes of chlorination correlated more closely with kill data. This led to OT analysis of sewage treated with chlorine 5 minutes at 45°C. This test also correlated more closely with disinfection data than the 5 minute, 28°C test.

Sewage dosed with enough chlorine to give a residual OT value of 0.5 ppm gave satisfactory kill rates, particularly if the test was made after 20 minutes of sewage treatment at room temperature (28°C) or 5 minutes at 45°C. Values in the 1.0 ppm range, requiring little more applied chlorine than for the 0.5 ppm value, would assure extremely high kill rates in the Hyde Park sewage.

OT tests have not been made by us in cold sewage but it is clearly indicated that such tests will be unreliable. Cold sewage will have to be warmed during chlorine treatment or held an excessive time period if reliable demand figures are to be obtained.

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1. Henkelekain, H., Day, Robert, and Manganelli, Raymond. Disinfection of Wastes by Chlorination, Ind. and Eng. Chem., 45, 1004 (1953).

Sewage with a high amino-N content should have a more severe chlorine treatment (longer time and/or higher temperature) before determining the chlorine demand than sewage with a low amino nitrogen content.

It has been noted in two experiments that very septic sewage, with an extremely high chlorine demand, gave extremely high killing rates when adjusted to a low OT residual value. The severe microbial treatment probably lowered the amino acid level to an extremely low figure, a condition accounting for the high rate.

IX. TEMPERATURE EFFECT

Some time must be given to the study of temperature effects. It is practically certain that more chlorine and/or a longer contact time must be used at low temperature than at high temperature to get satisfactory disinfection. It will be of the greatest importance to determine demand values over an extended time period or by an elevated temperature procedure when dealing with cold sewage.

X. CHLORINATION CATALYSTS

Ferric iron supplements failed to improve chlorination efficiency in two experiments. Copper at two parts per million was associated with a considerably improved killing rate. The catalytic influence of metals on chlorination appears to be very much less than with oxidation, where they have marked influence. Study of the catalytic effects of metals was held in abeyance when preliminary experiments indicated that proteinaceous components were a far more important factor.

XI. MIXING CHLORINE WITH SEWAGE (~~Fig 10~~)

Thorough mixing of disinfectant and sewage is important for achieving a uniform killing rate in a sewage sample. If mixing is inadequate, regions with little or no chlorine will permit survival of bacteria. A sample experiement has demonstrated this factor.

Sewage was inoculated with *E. coli* and treated with 3.75 ppm of Cl_2. A control sample was mixed immediately and thoroughly after chlorination. A test sample was dosed with chlorine by

pipetting 2.5 ml of 150 ppm Cl_2 into 100 ml of inoculated sewage, with delay of mixing until sampling time. Plate counts are in Table 1. It is clearly evident that thorough mixing is required immediately after chlorination. Some mixing occurred as a result of the pipetting procedure; otherwise, no disinfection could have occurred in the sample.

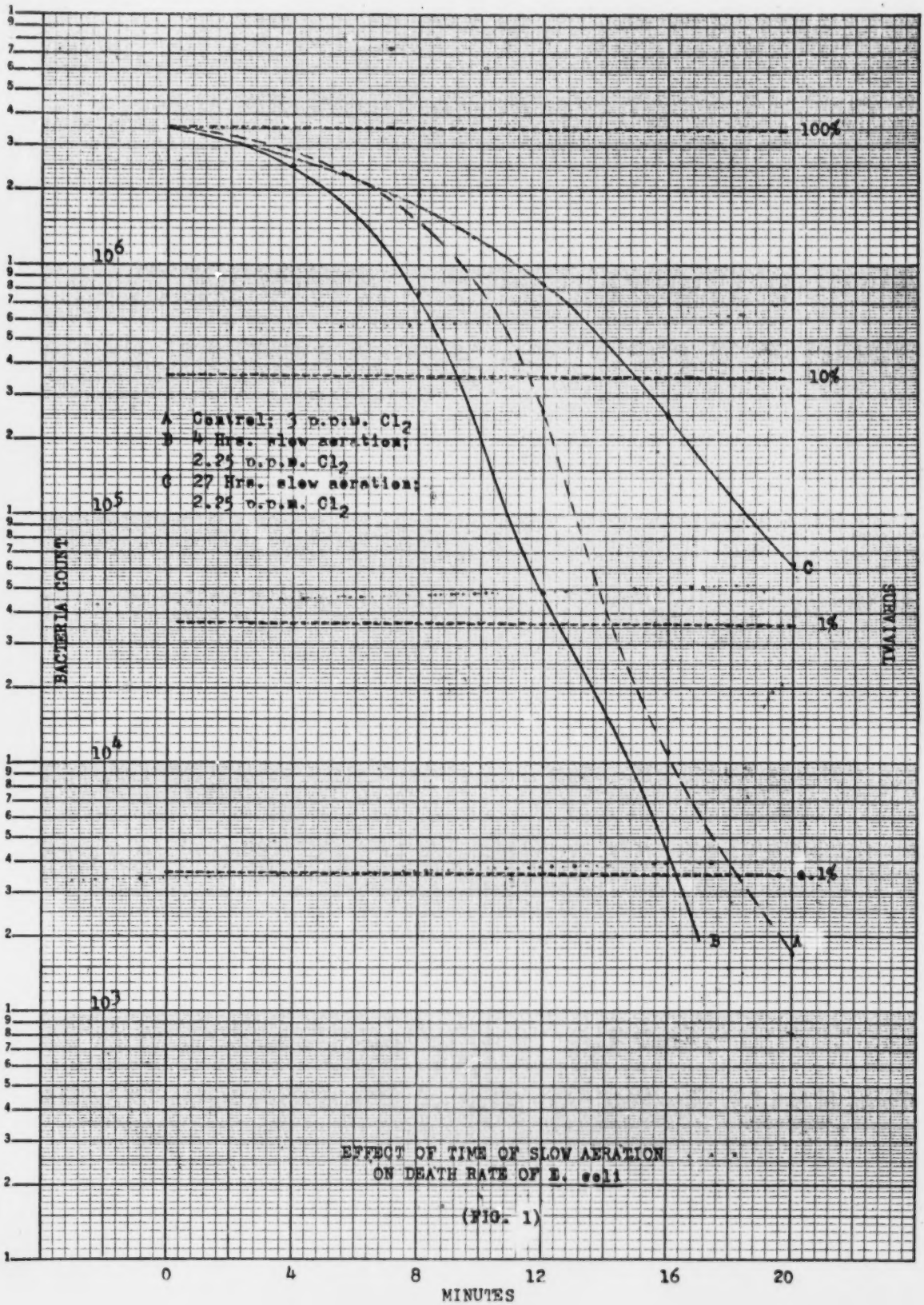
Some "mixing error" probably occurs throughout these experiments due to killing in intensely treated regions prior to complete dispersion of the chlorine in the treated sewage. This error has not been of serious proportion and undoubtedly could be eliminated by the practice of vigorous mechanical agitation during chlorine introduction. Mixing in the plant is not as easy as in the laboratory. Equipment of doubtful efficiency should be checked through actual disinfection data before approval.

II. SUMMARY: l.c. continued from page 1.

An activated sludge developed in the laboratory subsequent to this work is oxidizing sewage with almost no nitrite accumulation, whereas, the pilot plant sludge utilized in these studies invariably induced nitrite accumulation. The nitrite-free effluent has a much lower chlorine demand than the nitrite contaminated effluent. In the only survival study made with the nitrite-free effluent, chlorination of the effluent was more effective than chlorination of the original sewage.

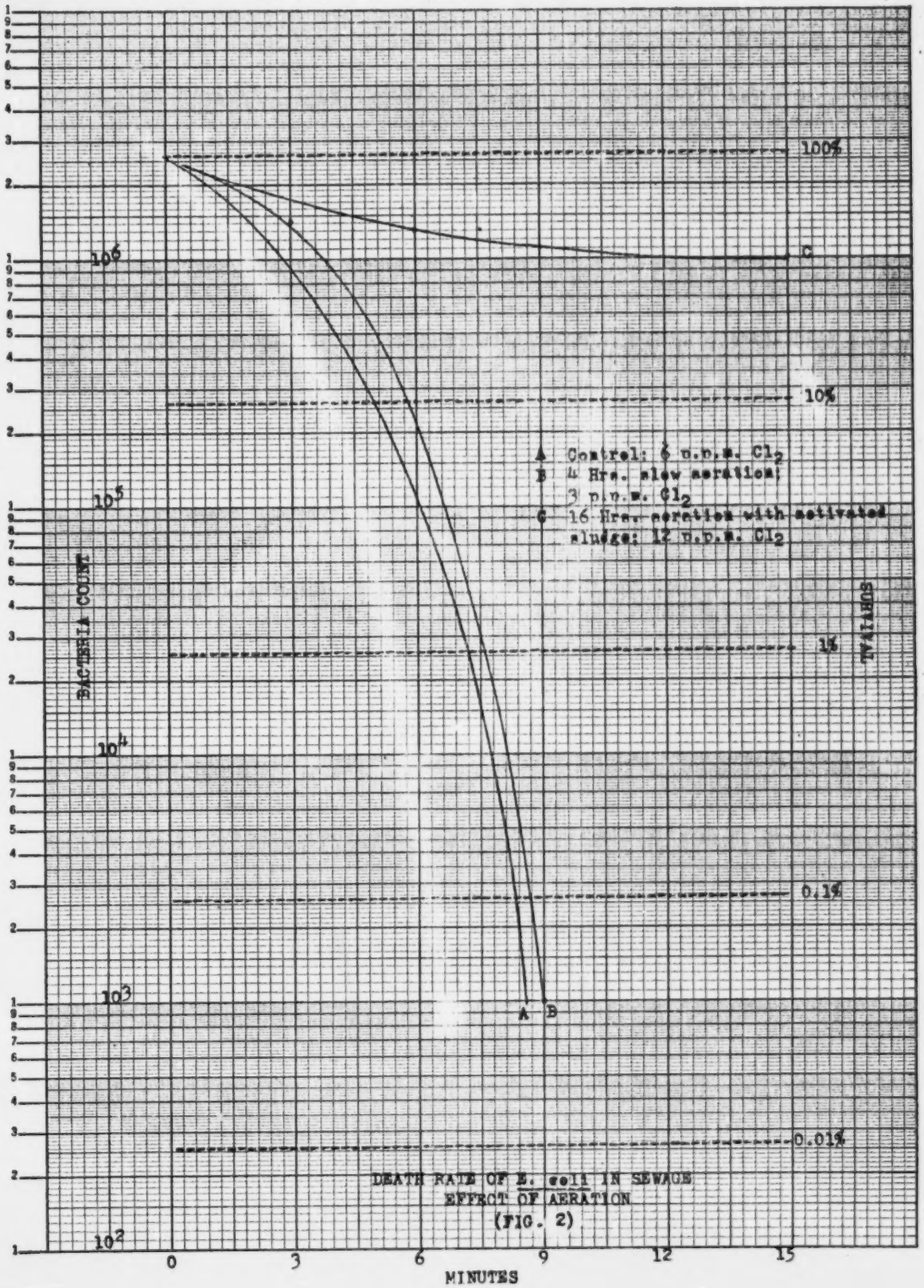
Table 1. VARIATION IN CHLORINATION EFFICIENCY WITH STIRRING

Minutes of Chlorination	Stirred Control	Unmixed Sample
0	248×10^4	248×10^4
3	152×10^4	___
6	70×10^4	___
9	35×10^3	___
12	29×10^2	___
15	< 100	___
18	< 100	35×10^4

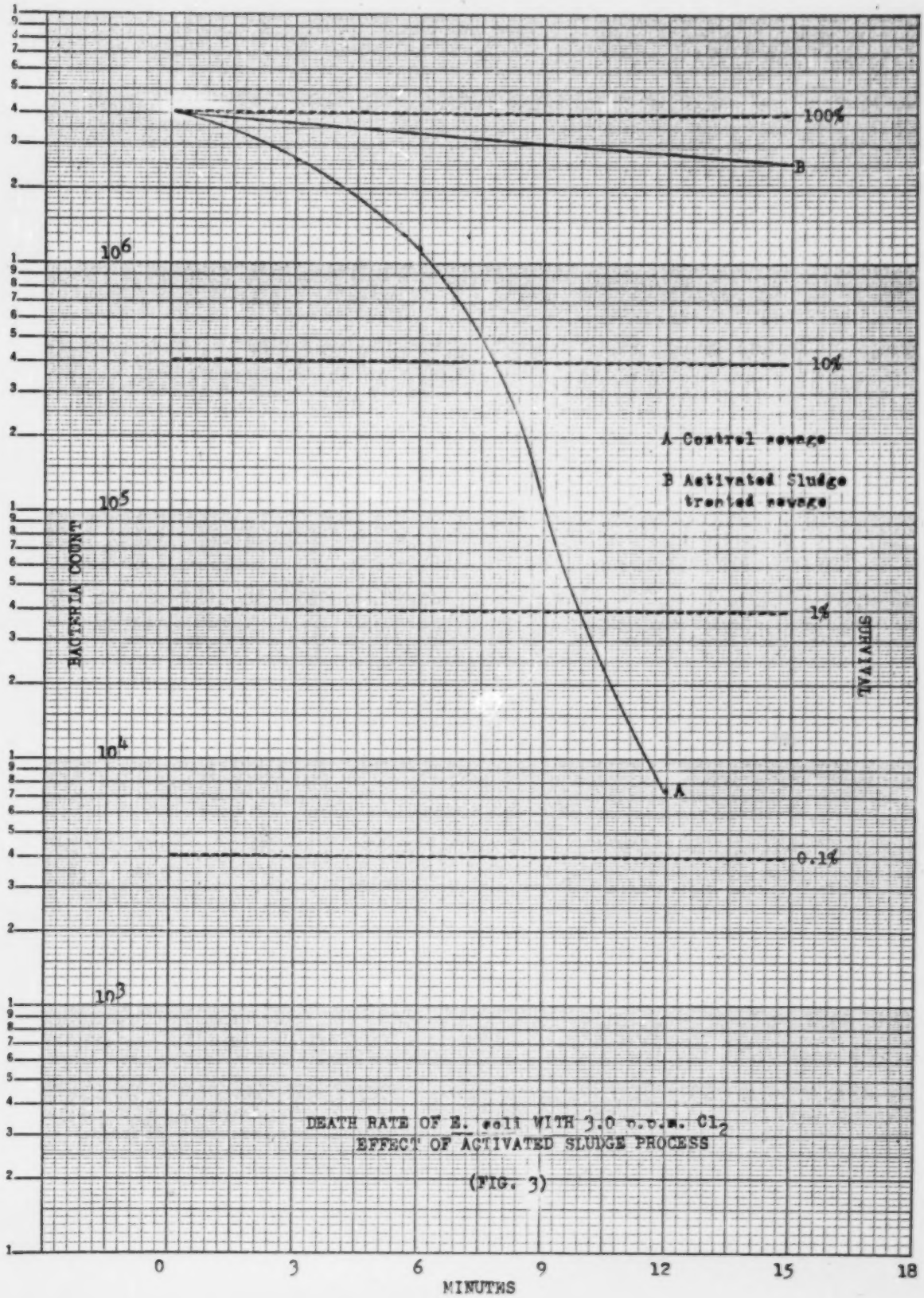


EFFECT OF TIME OF SLOW AERATION ON DEATH RATE OF E. coli

(FIG. 1)

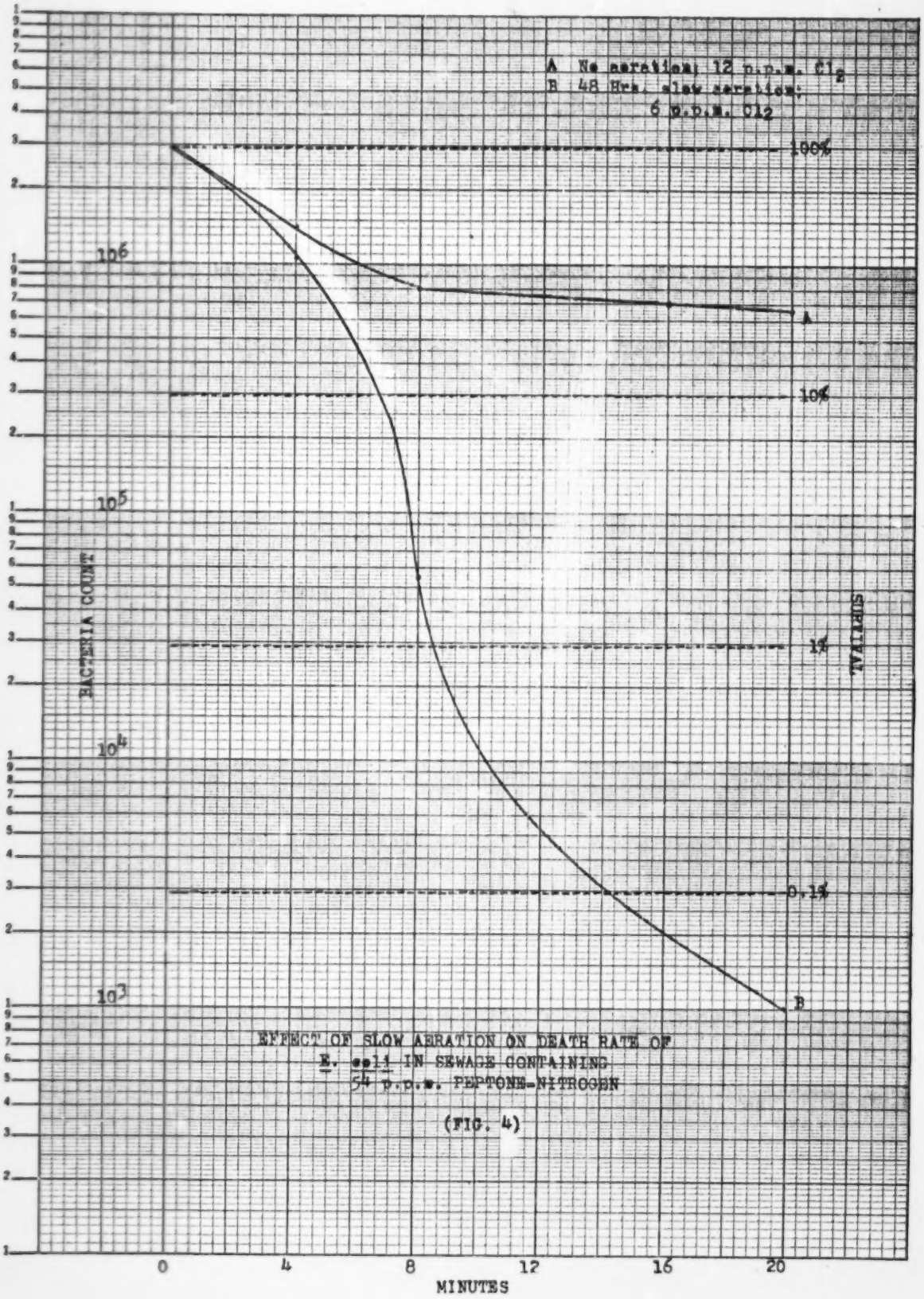


DEATH RATE OF E. coli IN SEWAGE
EFFECT OF AERATION
(FIG. 2)



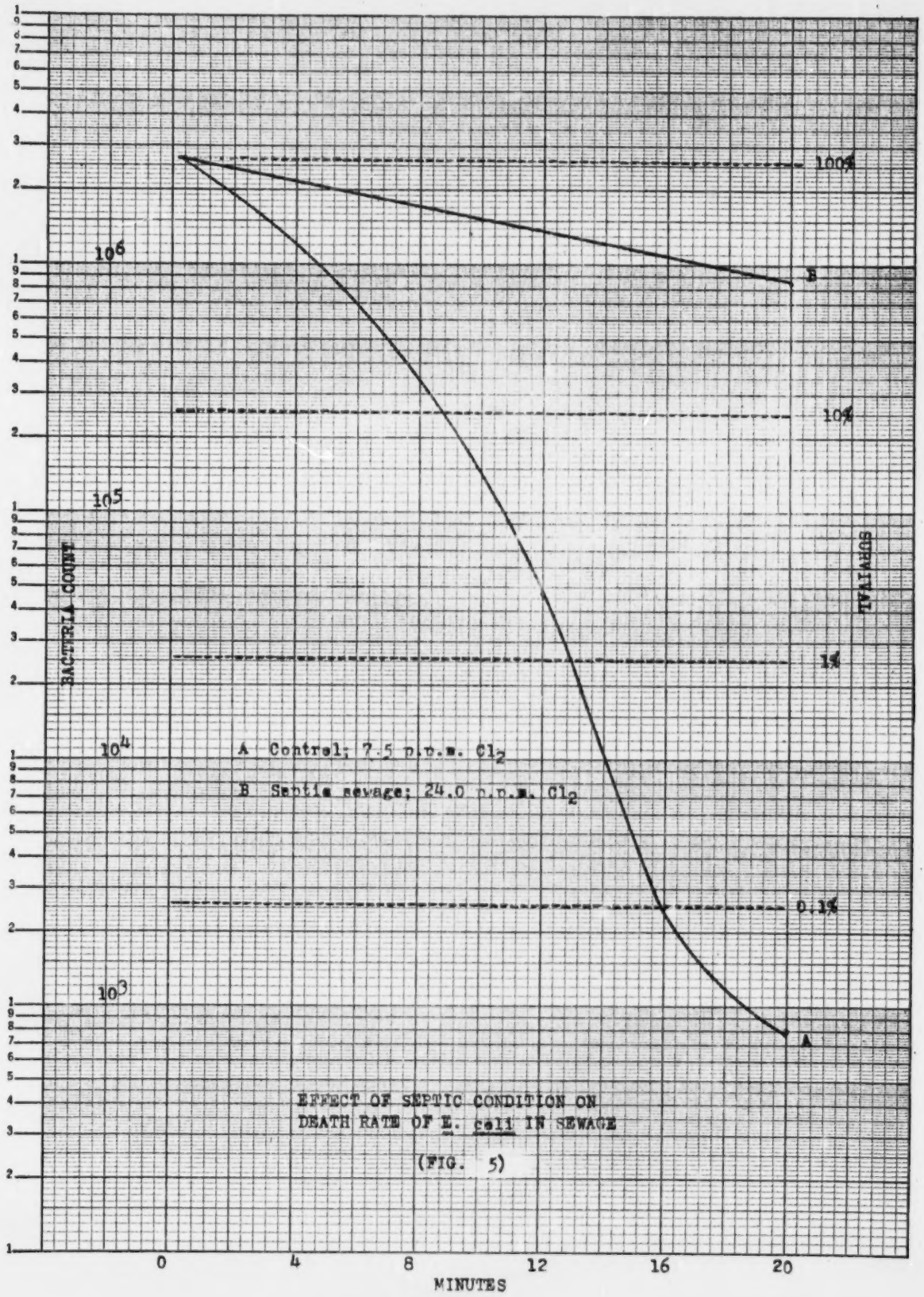
DEATH RATE OF E. coli WITH 3.0 p.p.m. Cl_2
EFFECT OF ACTIVATED SLUDGE PROCESS

(FIG. 3)



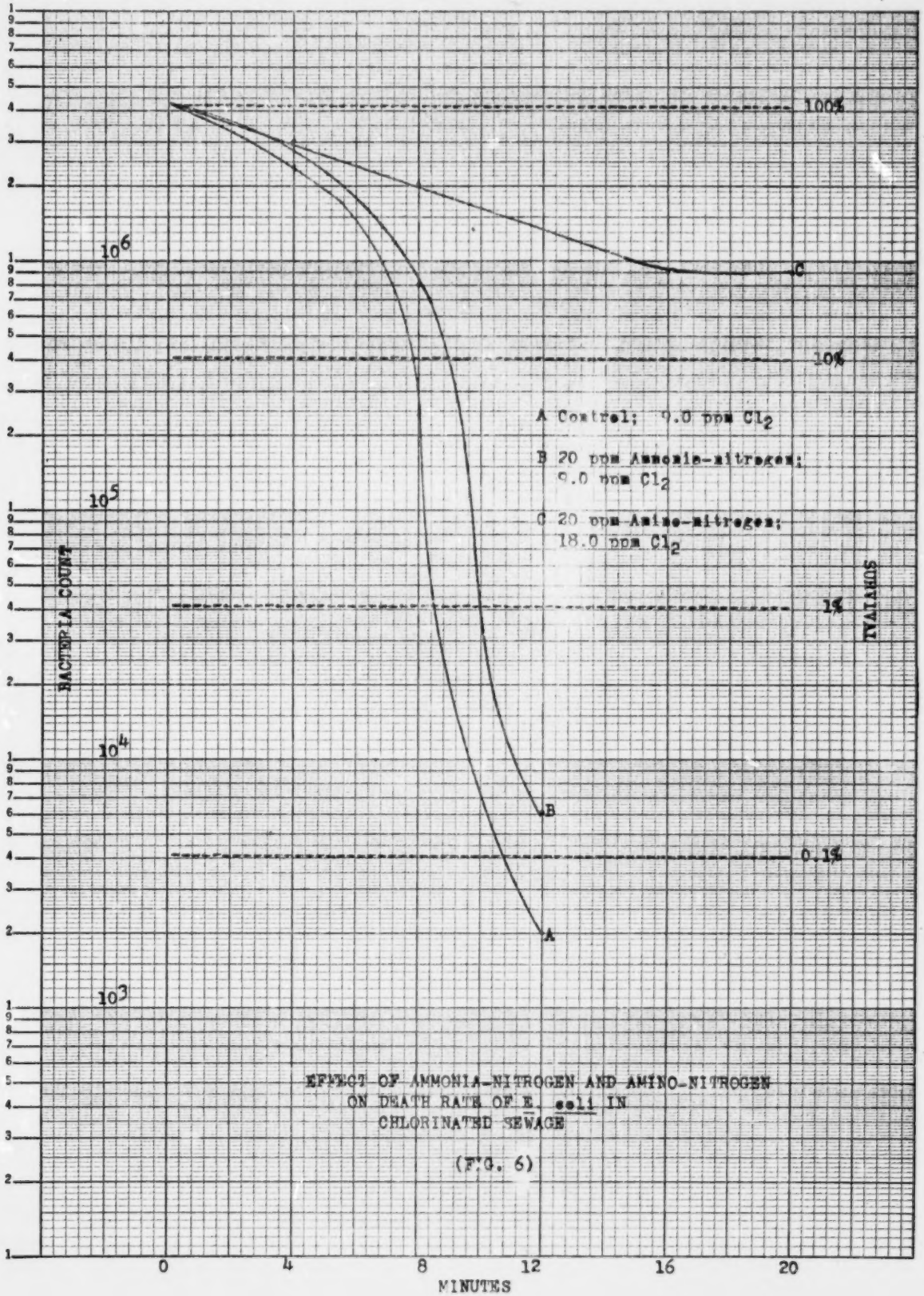
EFFECT OF SLOW AERATION ON DEATH RATE OF
E. coli IN SEWAGE CONTAINING
54 p.p.m. PEPTONE-NITROGEN

(FIG. 4)



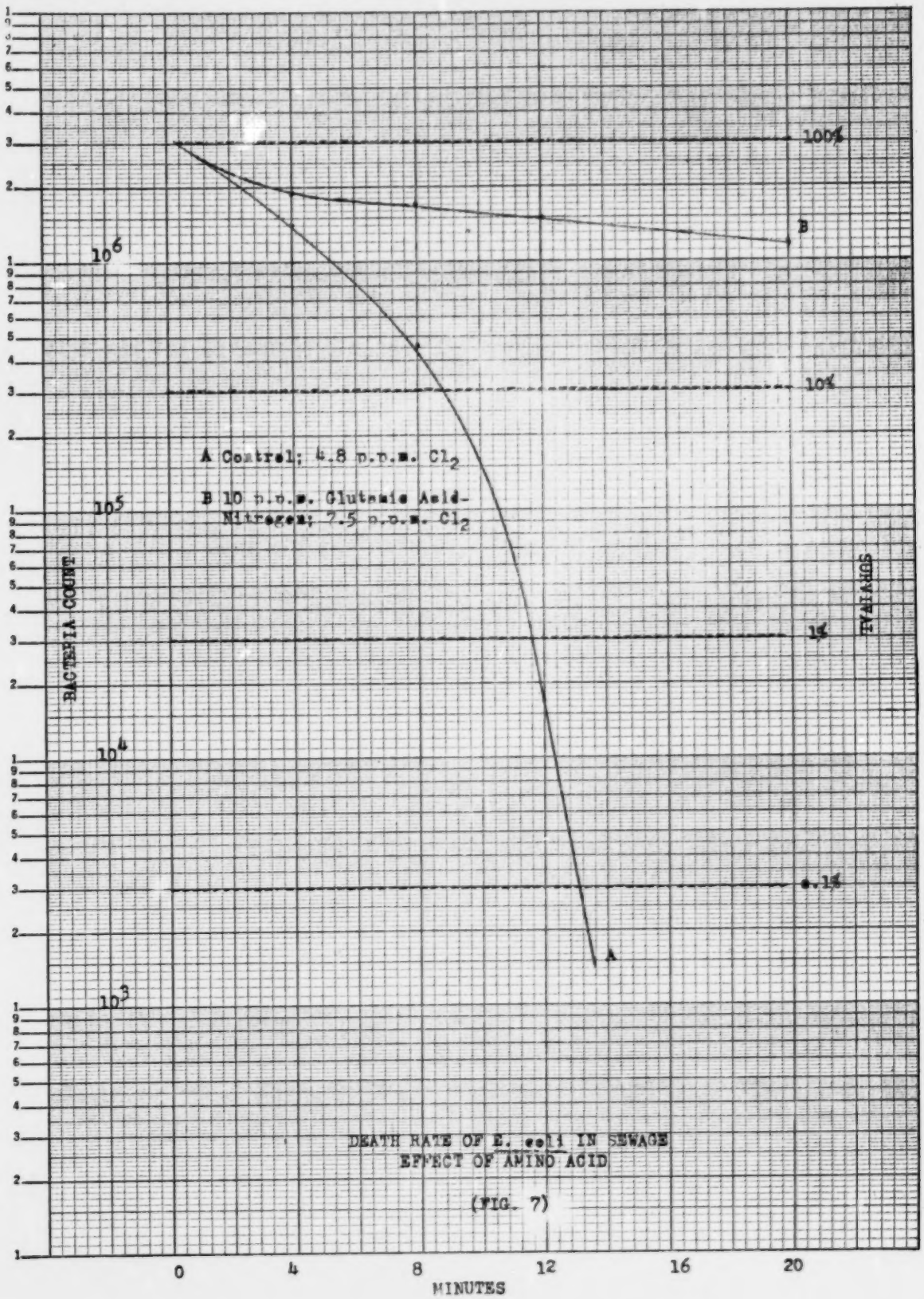
EFFECT OF SEPTIC CONDITION ON DEATH RATE OF E. coli IN SEWAGE

(FIG. 5)



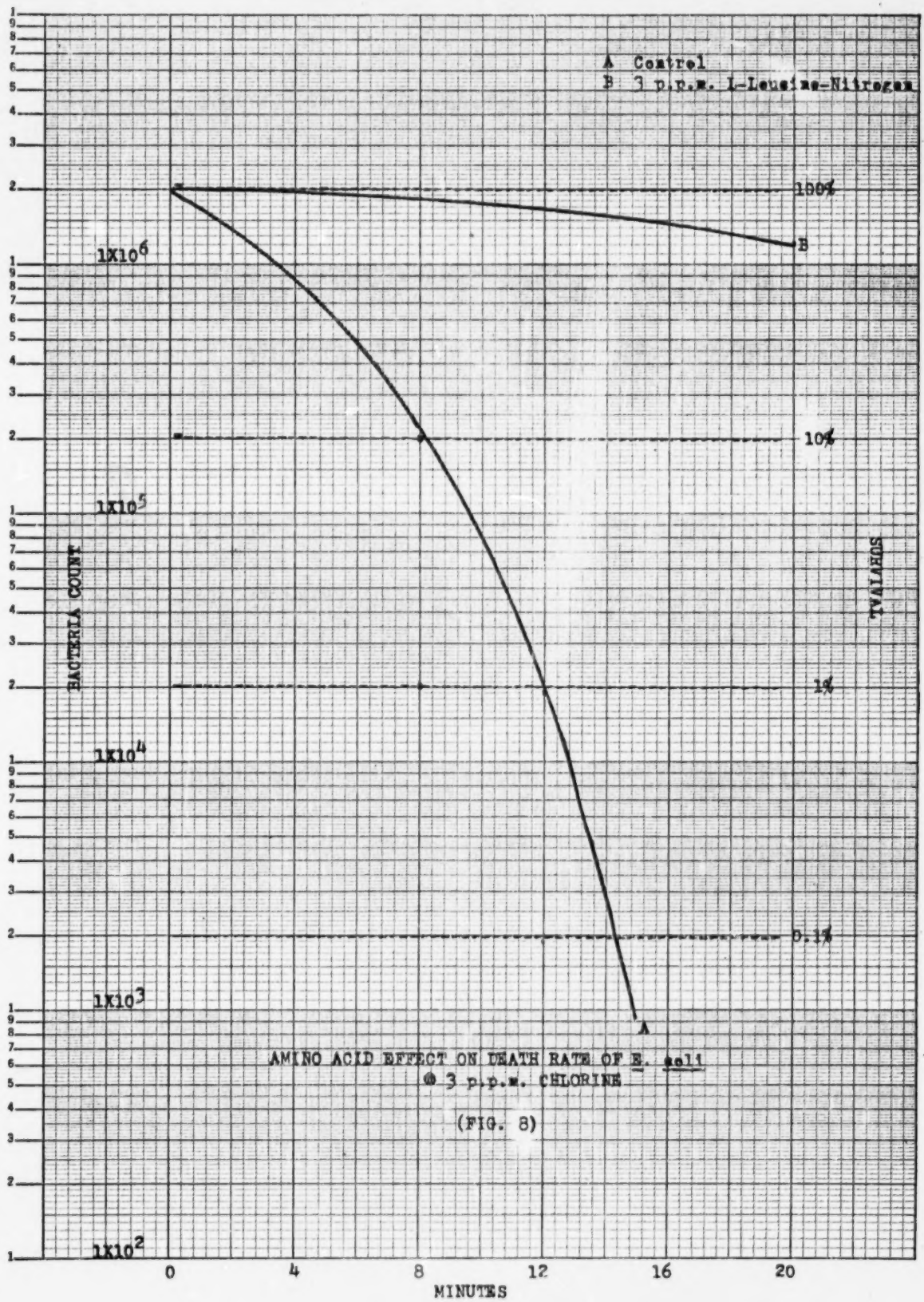
EFFECT OF AMMONIA-NITROGEN AND AMINO-NITROGEN ON DEATH RATE OF E. coli IN CHLORINATED SEWAGE

(FIG. 6)



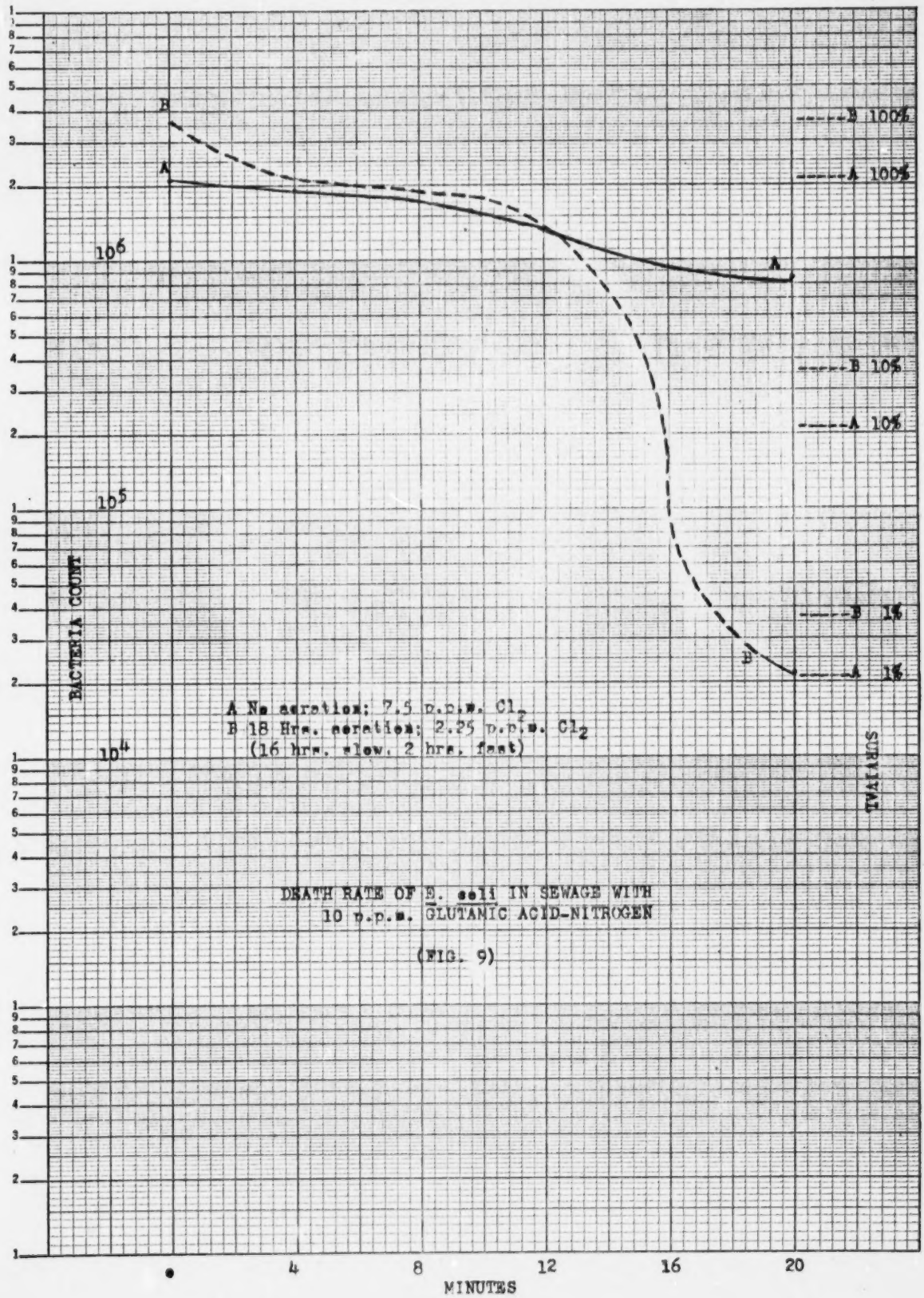
DEATH RATE OF E. coli IN SEWAGE
EFFECT OF AMINO ACID

(FIG. 7)



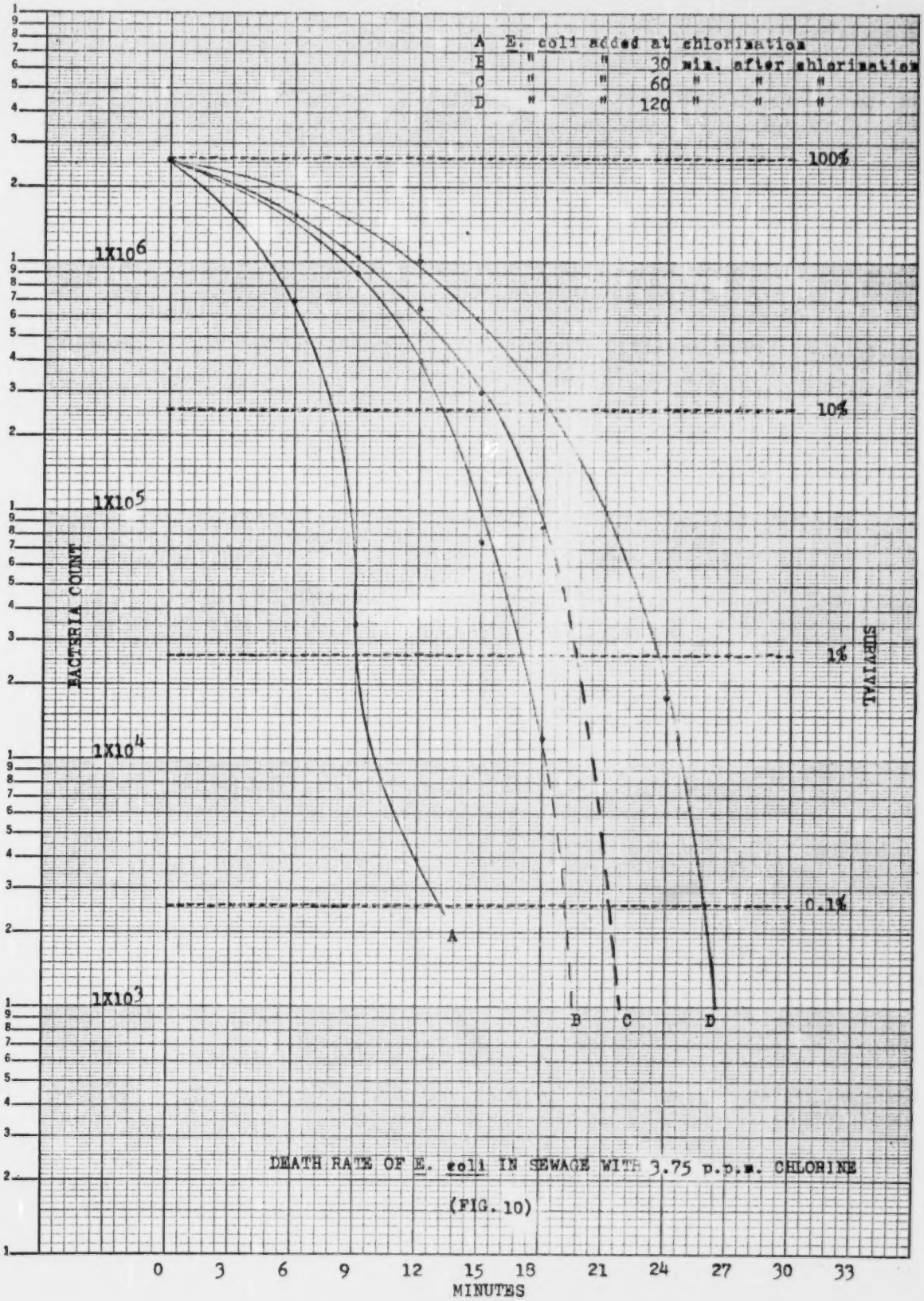
AMINO ACID EFFECT ON DEATH RATE OF E. coli
@ 3 p.p.m. CHLORINE

(FIG. 8)



DEATH RATE OF E. coli IN SEWAGE WITH 10 p.p.m. GLUTAMIC ACID-NITROGEN

(FIG. 9)



DEATH RATE OF E. coli IN SEWAGE WITH 3.75 p.p.m. CHLORINE

(FIG. 10)